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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Metal Composite and Electrolytic method of making same

We, CLEVITE CORPORATION, a corporation organised and existing under the laws of the State of Ohio, United States of America, of 17000 St. Clair Avenue, Cleveland, Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention provides a method of treating metal so as to improve its power of adhesion to a resinous substrate, the method involving the electrolytic deposition on the surface of the metal of an adherent nickeliferous coating under such conditions that the coating has a greyish matte appearance which is best described as suede-like; while not bright, the coating has a certain sheen or 'life', so that it is not exactly dull. While described below principally in its application to metal foils, the invention may be applied to foils, sheets or articles of nickel, nickel alloy, copper, or copper alloy.

15 The invention is particularly useful in the field of printed circuits, and particularly printed circuits which in normal use are submitted to temperatures which approach or exceed the melting of ordinary solder as is commonly used with printed circuits. As is known in the art, printed circuit boards are of laminar structure including a resinous substrate, for example, a fibre reinforced epoxy resin, an adhesive layer, or "sticker sheet", and a foil layer formed or formable (as by etching) to a predetermined electrical circuit. The aforementioned layers are pressed together at high pressure, for example, 1300 p.s.i. and at a temperature sufficient to soften the "sticker sheet", e.g., about 300°F, the adhesive hardening upon subsequent cooling.

20 While nickel foil has been used prior to this time in printed circuitry, the temperature sensitivity of the adhesive and/or the plastic backing sheet has generally made such printed circuits unsatisfactory for high temperature

applications. The epoxy resins are able to withstand elevated temperatures much better than, for example, the polyvinyl chloride resins, and are, therefore, desired for such high temperature applications. However, the adhesion of nickel to this adhesive is not satisfactory, and it is to the solution of this problem that the present invention is primarily directed. With copper foil, which has also been used extensively in printed circuitry, higher strength can be obtained with welded connections than with soldered connections, especially under high vibration conditions. Again, temperature sensitivity is a problem in view of the higher temperatures in forming the connections.

25 The invention allows any nickel, nickel alloy, copper, or copper alloy surface to be improved in respect of its adhesion to resinous substrates, and particularly glass fiber reinforced epoxy resins. However, for best results, we prefer to utilize electroformed nickel or copper foil having a thickness of from one to five mils. Rolled foil, i.e., foil produced by rolling a nickel or copper billet, may also be used, but better results are obtained with this material if it is preliminarily etched to remove the worked surface. The methods of producing electroformed nickel and copper foils and rolled nickel and copper foils are well known in the art and need not be detailed herein. It is preferred that the metal surface to be treated in accordance herewith shall be clean, and this can normally be achieved by a water rinse. If the metal to be treated in accordance herewith has been exposed to organic matter, or contains residual dirt or oil, for example, it should be degreased prior to treatment in accordance herewith. Best results are obtained with a freshly electrodeposited foil which is physically and chemically clean as results from a clean water rinse following the electroformation thereof. Cleaning may be effected electrolytically, or mechanically, as by the use of very finely divided magnesium oxide.

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- Clean nickel foil, or copper foil, for example, is then introduced into an electrochemical treating cell wherein it is rendered electro-negative with respect to a relatively electro-positive electrode, which is preferably non-consumable. A suitable material for this anode is platinized titanium, but carbon or any non-consumable electron conductor may be used. The electrodes of the cell (i.e. the foil, or other workpiece, and the anode) are disposed in confronting, preferably parallel relation and are so sized and configured that the distance between the electrodes is substantially the same at all points. The foil may be continuously supplied to the cell and bath from a supply roll at a rate such that the exposure time of each part of the foil will be equivalent to that obtained in a static system.
- The external circuit of the cell includes any suitable source of direct current, for example, a battery, or a D.C. generator.
- The spacing between the electrodes is somewhat critical, although spacing and time are related, one being directly proportional to the other. In other words, the greater the spacing between the electrodes, the greater the time of exposure at a given current density in order to achieve the desired result. It has been found that an optimum distance is from 1.5 to 2.5 inches in a static bath. The electrodes are desirably of like size and configuration, and are maintained in substantially parallel relationship for the greatest uniformity of treatment of the foil or other workpiece. If the article to be treated is cylindrical, a concentrically disposed annular non-consumable anode is employed. A suitable voltage for the external circuit is 6 volts.
- The internal circuit of the cell is composed of the inert non-consumable anode, the nickel or copper cathode, and the respective interfaces between the electrodes and an ion-containing and conducting medium which is disposed therebetween. The ion-conducting medium for most purposes, is ordinary tap water or preferably, demineralized water. A supply of nickel ions in the medium is provided by a water soluble salt of nickel. Suitable materials include nickel chloride ($6\text{ H}_2\text{O}$), nickel sulfate, nickel ammonium sulfate, nickel acetate, and nickel sulfamate. Also included in the ion-containing and conducting medium is ammonium chloride or ammonium bromide. The remaining ammonium halides are not satisfactory for the purposes of the present invention. Alkali metal halides and alkaline earth metal halides also are not suitable for use as a replacement for the ammonium chloride or ammonium bromide. The ion-containing and conducting medium may be used until the nickel concentration falls below the point where good results are obtained, i.e., below about 3 grams per liter. The spent medium may be restrengthened with nickel and reused,
- and may if desired, be utilized as a continuously circulating system.
- The concentration of nickel in the ion-containing and conducting medium should be in the range of from 3.5 to 15 grams of nickel per liter, calculated as the metal. This amounts to from about 15 to about 60 grams per liter of nickel chloride as the hexahydrate. The preferred concentration of nickel is in the range 10 to 15 grams per liter. The concentration of the ammonium chloride should be in the range of from 75 grams per liter as a minimum up to the maximum limit of solubility of ammonium chloride in the ion-containing and conducting medium. Normally from 80 to 120 grams per liter of the ammonium chloride will be satisfactory. A stoichiometrically equivalent amount of the bromide may be used in place of the chloride.
- The electrochemical reaction is carried out for a period of time in the range of from 0.2 minutes to 3 minutes. The temperature of the ion-containing and conducting medium is about room temperature, and if necessary, cooling means are provided to maintain the temperature at about 70°F. The pH of the solution is within the range of from 2.0 to 6.0 and the current density at which the electrochemical treatment of the surface is carried out is in the range of from 50 to 150 amperes per square foot. When nickel chloride hexahydrate is used as the source of the nickel ions, the preferred pH of the ion-containing and conducting medium is approximately 6. With a nickel sulphate as the source of the nickel ion, the pH will generally be between 2 and 3.
- In carrying out the method of the present invention, it is not desired to obtain a smooth or sound nickel metal plate on the electro-formed nickel or copper surface. The conditions which are employed in carrying out the present method constitute a departure from normal nickel plating procedures. By comparison with the conditions required to produce a sound nickel plate, the pH is too high, the concentration of the metal ion is too low, and the temperature of the plating bath is also too low. The current density employed is abnormal for the nickel concentration in the ion-containing and conducting medium, and the concentration of the ammonium ion in the solution is most unusual. On the other hand, it is not desired to produce a powdery, easily removable deposit on the surface of the metal being treated. The finish which is obtained in a properly treated surface in accordance with this invention is suede-like, and the coating which is applied is strongly bonded to the nickel or copper surface. If the time of exposure is too long, or the current density is too high, or there is no ammonium ion present, then the result is not satisfactory for the purposes of this invention. If

the temperature is increased too much, then a sound or smooth metal plate is secured. If the nickel concentration is too high, then a smooth metal plate is secured. Within the limits stated herein and in keeping with the relationships among the parameters as stated, desired results are secured.

It is not completely understood what transpires at the interface between the nickel or copper cathode and the ion-containing and conducting medium, and the composition of the electrocathodically formed nickeliferous coating is not known. It is believed that the pH change which occurs at the interface between the cathode and the nickel ion-containing and conducting medium affects the deposition of nickel metal, possibly including or occluding nickel oxide, or hydroxide. The coating produced is accordingly referred to herein as a "nickeliferous" coating, rather than as a nickel coating. On treating the metal surface in accordance with this invention, the surface area is increased. The deposit is especially well adapted to coact with a resinous substrate, such as an epoxy resin, to improve adhesion. The surface produced on the nickel or copper substrate being of increased area and rough character results in improved adhesion to the "sticker sheet", and there also appears to be an enhancement of chemical adhesion. It is believed that the nature of the surface produced results from the lowering of the cathode current efficiency from that which is normally required to plate good sound nickel on a nickel or a copper substrate.

After the electrochemical treatment of the surface is completed, the foil, sheet or article is rinsed, and may desirably be given a chromate dip. This consists in immersing the treated surface for (say) 15 seconds in an aqueous chromic acid at a concentration of from 0.15 to 0.5 grams per liter, e.g. 0.25 grams per liter.

When nickel or copper foil which has been treated in accordance herewith is laminated with an epoxy resin through an intermediate "sticker sheet", it is possible to obtain adhesions of from 5 to 16 pounds per inch, as determined by the standard N.E.M.A. procedure for determining bond strengths of laminated metallic foils on non-metallic substrates.

The manner in which the bond strength

measurements are made is as follows: a six inch square of nickel foil, for example, treated in accordance with this invention is cemented to a six inch square of epoxy resin by interposing a "sticker sheet" and subjecting the assembly to the influence of heat (302°F.) and a pressure of approximately 1300 p.s.i. After allowing the adhesive to harden by cooling, score lines one inch apart are struck across the surface, penetrating through the nickel foil. The edge of the one inch strip of nickel foil is turned back by stripping from the surface a short distance, and clamped in a tensiometer. The tensiometer is so adapted and constructed as to exert a steady pull at right angles to the surface of the metal foil-resin laminate providing a continuous reading in terms of pounds of pull per inch of width of the force required to strip the foil from the resin.

Electroformed nickel foil, or rolled nickel foil, which has not been treated in any way when tested in the manner aforesaid exhibits substantially no adhesion to the resinous substrate. However, when such foils have been treated in accordance with the present invention, adhesions in the range of from 5 to 16 pounds per inch on the same substrate are obtained.

The following table contains specific examples of conditions employed to treat electroformed nickel foil in accordance with the present invention and shows the bond strength obtained when the foil so treated was laminated as described above to G-10 Epoxy glass, being a glass fibre reinforced epoxy resin of a commercial grade used for printed circuits. The pairs of figures joined by a hyphen which appear in the table under bond strength show the limits of the tensiometer readings (in pounds per inch) obtained during the testing in the manner described above of a single specimen. In some cases results are given for two or more specimens which had received the same treatment. For purposes of comparison the table also includes the result of similar bond strength tests on electroformed nickel foil which had received no treatment whatever and on foil which had been treated only by giving it a chromate dip.

Treatment	Bond Strength
Nil	Nil
15 sec. chromate dip	1.6 — 2.8
1. Nickel chloride hexahydrate, 50 grams/liter ammonium chloride 100 grams/liter pH 6.0	
(a) Current Density 100 a.s.f. (amperes per square foot) Time — 1 minute 15 sec. chromate dip 0.25 grams/liter	13.6 — 15.0 11.0 — 11.4 14.0 — 15.4 11.6 — 12.8 12.0 — 12.6
(b) Current Density 150 a.s.f. Time — 15 seconds 15 sec. chromate dip	15.0 — 16.0 12.2 — 13.2
2. Nickel chloride hexahydrate, 50 grams/liter ammonium chloride 100 grams/liter pH 6.0	
(c) Current Density 100 a.s.f. Time — 1 minute	10.0 — 11.2 9.6 — 10.2 12.8 — 13.8
(b) Current Density 150 a.s.f. Time — 15 seconds	13.4 — 14.0 10.6 — 11.8
3. Nickel sulfate 25 grams/liter ammonium chloride 100 grams/liter pH 2.2 — 2.5	
(a) Current Density 100 a.s.f. Time — 1 minute 15 sec. chromate dip	12.0 — 12.6 9.8 — 11.2 11.4 — 12.4
(b) Current Density 150 a.s.f. Time — 15 seconds 15 sec. chromate dip	9.0 — 10.4
4. Nickel ammonium sulfate 50 grams/liter ammonium chloride 100 grams/liter pH 3.5	
(a) Current density 100 a.s.f. Time 1 minute (i) no chromate dip (ii) 15 sec. chromate dip	8.0 — 9.0 9.6 — 11.2
(b) Current density 150 a.s.f. Time 15 sec. (i) no chromate dip (ii) 15 sec. chromate dip	5.0 — 6.6 7.6 — 9.0

Treatment	Bond Strength
5. Nickel ammonium sulfate 25 grams/liter ammonium chloride 100 grams/liter pH 3.5	
(a) Current density 50 a.s.f. 2 min. — 15 sec. chromate dip	11.0 — 11.4
(b) Current density 100 a.s.f. 1 min. — 15 sec. chromate dip	7.6 — 8.8
(c) Current density 150 a.s.f. 15 sec. — 15 sec. chromate dip	6.6 — 7.4

Examples 1 to 5 are treatments on nickel foil. The same solutions and conditions may be used in depositing a nickeliferous coating on copper.

- After the deposition of a nickeliferous coating on a nickel or copper substrate as described above, a sound coating of nickel may be deposited over the nodularized surface which results from the treatment above described, thereby encapsulating the nickeliferous projections. It has been found that this improves the strength of such projections and gives better handling characteristics to the foil, sheet, or article treated. Solutions and conditions for accomplishing the encapsulation operation include conventional sound nickel metal plating baths, plating conditions, and plating apparatus.
- WHAT WE CLAIM IS:—**
1. A metallic composite comprising a metal substrate of nickel, nickel alloy, copper, a copper alloy and an electrocathodically formed nickeliferous coating adhered thereto, said coating having a suede-like appearance and being formed by electrolytically depositing nickel onto said substrate from an aqueous solution of from 3.5 to 15 grams of nickel per liter of solution derived from a water soluble nickel salt, and from 75 grams per liter of solution to the limit of solubility in said solution of ammonium chloride, or a stoichiometrically equivalent amount of ammonium bromide, said solution having a pH of from 2 to 6, said deposition being carried out at room temperature and at a current density of from 50 to 150 amperes per square foot, for a period of from 0.2 minute to 3 minutes.
 2. A composite in accordance with claim 1 in which the metal substrate is nickel foil.
 3. A composite in accordance with claim 1 in which the metal substrate is copper foil.
 4. A composite in accordance with claim 2 in which the nickel foil is electroformed nickel foil.
 5. A composite in accordance with claim 4 in which the coating is formed upon the as

- plated surface of said electroformed nickel 45 foil substrate.
6. A composite in accordance with claim 1 in which the water soluble nickel salt is nickel chloride hexahydrate.
 7. A method for electrocathodically treating a surface of nickel, nickel alloy, copper or copper alloy to improve its adhesion to a resinous substrate which comprises the steps of:
 - (a) disposing said metal surface in substantially uniformly spaced confronting relation to an electron conducting member;
 - (b) disposing between and in interface-forming relation with said metal surface and said electron conducting member, an internal circuit forming aqueous ion-containing and conducting medium including per liter of solution from 3.5 to 15 grams of nickel derived from a nickel salt soluble in said solution, and from 75 grams to the limit of solubility in said solution of ammonium chloride, or a stoichiometrically equivalent amount of ammonium bromide, said medium having a pH of from 2 to 6;
 - (c) rendering said metal surface electro-negative relative to said electron conducting member; and
 - (d) passing an electric current through the internal circuit at a current density of from 50 to 150 amperes per square foot for a period of time of from 0.2 to 3 minutes at about room temperature to deposit nickeliferous coating on said metal surface.
 8. A method in accordance with claim 7 wherein the metal surface is spaced from said electron conducting member from 1.5 to 2.5 inches.
 9. A method in accordance with claim 7 wherein said metal surface is nickel foil.
 10. A method in accordance with claim 7 wherein said metal surface is copper foil.
 11. A method in accordance with claim 9

- wherein said foil is continuously moved relative to said electron conducting member.
12. A method in accordance with claim 10 wherein said foil is fed past said electron conducting member from a supply roll.
- 5 13. A method in accordance with claim 7 wherein said electron conducting member is a non-consumable electrode.
14. A method in accordance with claim 13 wherein said electrode is a platinized titanium anode.
- 10 15. A method in accordance with claim 7 wherein the nickel salt is nickel chloride hexahydrate.
- 15 16. A method in accordance with claim 7 additionally characterized by the step of dipping the electrocathodically treated metal surface in an aqueous bath containing chromic acid at a concentration of from 0.15 to 0.5 20 grams per liter.
17. An ion-containing and conducting medium having a pH of from 2 to 6 and useful in forming an electrocathodically deposited nickeliferous coating on a nickel metal surface consisting essentially of:
- (a) from 10 to 15 grams of nickel per liter of ion-containing and conducting medium, said nickel being derived from a nickel salt soluble in said medium;
- (b) from 75 grams of ammonium chloride per liter of ion-containing and conducting medium to the limit of solubility in said medium or a stoichiometrically equivalent amount of ammonium bromide; and
- (c) water to make a liter of medium.
18. An ion-containing and conducting medium in accordance with claim 17 in which the nickel salt is nickel chloride hexahydrate.
19. A method in accordance with claim 7 which is additionally characterized by the step of encapsulating the nickeliferous coating with a coating of sound nickel.
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